Bis(succinimidato)copper(II) Complexes with Pyridine, Picolines and Lutidines

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Succinimidate, which is derived when succinimide (Fig. 1) loses a proton, forms a number of copper (II) complexes with different amines bound together. In a previous communication,1) a series of red bis(succinimidato)-bis(alkylamine)copper(II) complexes were examined, and the factors favoring the formation of these red copper(II) complexes discussed. In order to confirm and extend the conclusions previously derived, it was thought to be interesting to examine complexes of a similar type with other amines. The present paper deals with bis(succinimidato)copper(II) complexes combining pyridine, picolines and lutidines.

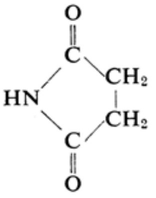

Fig. 1. Succinimide.

Experimental

Materials. — *Pyridine Complexes.* — [Cu(*sucim*)$_2$(*py*)(OH$_2$)] was prepared in violet, cubic crystals according to the method of Tschugaeff,2) where *sucim* and *py* denote a succinimidate ion and a pyridine molecule respectively. The crystals were stable in the atmosphere and were recrystallized from ethanol containing a few drops of pyridine.

Found: C, 43.9; H, 4.60; N, 11.6. Calcd. for $C_{13}H_{15}N_3O_5Cu$: C, 43.8; H, 4.24; N, 11.8%.

[Cu(*sucim*)$_2$(*py*)$_2$] was prepared, by a method similar to that used for [Cu(*sucim*)$_2$(*py*)(OH$_2$)], from 10 g. (0.1 mol.) of succinimide, 3 g. (0.05 g. atom) of copper powder, and 12 g. (0.15 mol.) of pyridine, with ethanol as a solvent. Since this compound was rather unstable in the atmosphere, the product was filtered in the dry air and stored in a tightly-closed bottle or in a desiccator containing sodium hydroxide. The crystals were recrystallized from an ethanol-pyridine mixture. The brown-red crystals, which were not quite free from the mother liquor, turned violet on exposure to the air, a co-ordinated pyridine molecule being replaced by a water molecule in the atmosphere. The compound was comparatively stable in the atmosphere when completely free from the mother liquor.

Found: C, 51.7; H, 4.50; N, 13.4. Calcd. for $C_{18}H_{18}N_4O_4Cu$: C, 51.7; H, 4.34; N, 13.4%.

Picoline Complexes. — [Cu(*sucim*)$_2$(α-*pic*)(OH$_2$)$\cdot$CH$_3$OH] was prepared from 3 g. (0.05 g. atom) of copper powder, 10 g. (0.1 mol.) of succinimide and 10 g. (0.1 mol.) of α-picoline by a procedure similar to that used for [Cu(*sucim*)$_2$(*py*)$_2$], except that 50 ml. of methanol was used as a solvent. The notation '*pic*' denotes picoline. The product was filtered in the dry air and dried over phosphorus pentoxide in a vacuum desiccator. Recrystallization was carried out from methanol containing a suitable amount of the amine. Since these crystals turned from blue to green in the atmosphere, the compound was stored in a desiccator over sodium hydroxide.

Found: C, 45.0; H, 5.45; N, 10.0. Calcd. for $C_{15}H_{21}N_3O_6Cu$: C, 44.7; H, 5.25; N, 10.4%.

[Cu(*sucim*)$_2$(α-*pic*)$_2$] was obtained from [Cu(*sucim*)$_2$(α-*pic*)(OH$_2$)$\cdot$CH$_3$OH]. An excess of [Cu$\cdot$(*sucim*)$_2$(α-*pic*)(OH$_2$)$\cdot$CH$_3$OH] was added to methylene dichloride containing a small amount of α-picoline, and the solution was stirred for two hours; the blue crystals of the starting complex changed to red microcrystals. The product was filtered in the dry air and dried over phosphorus pentoxide in a vacuum desiccator. Recrystallization of the compound was carried out from ethanol containing an excess of α-picoline. The brown-red color of these crystals soon turned green in the atmosphere. The compound, however, was comparatively stable in the air when completely free from the mother liquor.

Found: C, 53.9; H, 4.99; N, 12.8. Calcd. for $C_{20}H_{22}N_4O_4Cu$: C, 53.9; H, 4.97; N, 12.6%.

[Cu(*sucim*)$_2$(β-*pic*)$_2\cdot$2H$_2$O] was prepared by a method similar to the oxidation method of Tschugaeff, except that the filtration of the product was carried out in the dry air. The product consisted of deep-blue, needle-like crystals, which were hygroscopic. The crystal changed its color from deep-blue to red when stored for half a day over phosphorus pentoxide in a vacuum desiccator. The red compound is most probably [Cu(*sucim*)$_2$(β-*pic*)$_2$], which is considered to be formed by the removal of two co-ordinated water molecules from [Cu(*sucim*)$_2$(β-*pic*)$_2\cdot$2H$_2$O].

Found: C, 49.9; H, 5.29; N, 11.3. Calcd. for $C_{20}H_{26}N_4O_6Cu$: C, 49.8; H, 5.44; N, 11.6%.

Red crystals of [Cu(*sucim*)$_2$(β-*pic*)$_2$] were obtained from a methylene dichloride solution of [Cu(*sucim*)$_2$(β-*pic*)$_2\cdot$2H$_2$O]. When the solution was evaporated over phosphorus pentoxide in a vacuum desiccator, red crystals separated out. Since these

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1) S. Yamada and S. Miki, This Bulletin, **36**, 680 (1963).

2) L. Tschugaeff, *Ber.*, **38**, 2900 (1905).

red crystals turned blue immediately on exposure to the air, it was quite difficult to analyze the complex and to examine its properties. However, a comparison with other complexes of a $[\mathrm{Cu}(\mathit{sucim})_2(\mathit{pic})_2]$-type shows that the red product is most probably $[\mathrm{Cu}(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2]$.

$[\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2\cdot\mathrm{H_2O}]$ was easily prepared by a method similar to the oxidation method of Tschugaeff. The complex was obtained as violet-blue, cubic crystals which were stable in the atmosphere.

Found: C, 51.8; H, 5.22; N, 12.2. Calcd. for $\mathrm{C_{20}H_{24}N_4O_5Cu}$: C, 51.8; H, 5.21; N, 12.1%.

$[\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(\mathrm{OH_2})]$ was prepared by a procedure similar to that used for $[\mathrm{Cu}(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})_2]$, except that $[\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2\cdot\mathrm{H_2O}]$ was used in place of $[\mathrm{Cu}(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})(\mathrm{OH_2})\cdot\mathrm{CH_3OH}]$. The compound was obtained as violet microcrystals. The compound was comparatively stable in the atmosphere when completely free from the solvent or mother liquor.

Found: C, 44.4; H, 4.61; N, 11.8. Calcd. for $\mathrm{C_{14}H_{17}N_3O_5Cu}$: C, 45.3; H, 4.62; N, 11.3%.

$[\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2]$ was obtained in brown-red, plate-like crystals by a method similar to that used for $[\mathrm{Cu}(\mathit{sucium})_2(\mathit{py})_2]$, except that 14 g. (0.15 mol.) of γ-picoline was used in place of 12 g. of pyridine. On exposure to the atmosphere, the crystals changed into blue crystals of $[\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2\cdot\mathrm{H_2O}]$.

Found: C, 53.5; H, 4.88; N, 12.8. Calcd. for $\mathrm{C_{20}H_{22}N_4O_4Cu}$: C, 53.9; H, 4.97; N, 12.6%.

$\mathrm{Cu}(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(\mathrm{OH_2})_n\cdot\mathrm{CH_3OH}$ was obtained as deep-blue crystals by the same method as that used for $[\mathrm{Cu}(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})(\mathrm{OH_2})\cdot\mathrm{CH_3OH}]$. When exposed to the air, or when stored over phosphorus pentoxide in a vacuum desiccator, the product underwent decomposition. Accurate elemental analyses, therefore, were difficult, but the analyses agreed with the above formula, with *n* having a value between one and two.

Lutidine Complexes. — $[\mathrm{Cu}(\mathit{sucim})_2(2,4\text{-}\mathit{lut})_2]\cdot 0.5\mathrm{H_2O}$, in which the notation '*lut*' denotes lutidine, was obtained as red crystals by a method similar to that used for $[\mathrm{Cu}(\mathit{sucim})_2(\mathit{py})_2]$, except that 15 g. (0.15 mol.) of 2,4-lutidine was used in place of 12 g. of pyridine. On exposure to the air, the crystals gradually decomposed, finally forming a sky-blue powder.

Found: C, 53.8; H, 5.48; N, 12.3. Calcd. for $\mathrm{C_{22}H_{27}N_4O_{4.5}Cu}$: C, 54.7; H, 5.64; N, 11.6%.

$[\mathrm{Cu}(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2\cdot\mathrm{H_2O}]$ was obtained, by a method similar to the oxidation method of Tschugaeff, from 5 g. (0.05 mol.) of succinimide, 1.5 g. (0.025 g. atom) of copper powder, and 5.5 g. (0.05 mol.) of 3,5-lutidine. This complex formed blue plate-like microcrystals which were stable in the air.

Found: C, 53.2; H, 5.88; N, 11.5. Calcd. for $\mathrm{C_{22}H_{28}N_4O_5Cu}$: C, 53.7; H, 5.74; N, 11.4%.

Red crystals of $[\mathrm{Cu}(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2]$ were obtained by the same method as that used for $[\mathrm{Cu}(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2]$, except that $[\mathrm{Cu}(\mathit{sucim})_2(3,5\text{-lut})_2\cdot\mathrm{H_2O}]$ was used in place of $[\mathrm{Cu}(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2 2\mathrm{H_2O}]$. On exposure to the atmosphere, the compound readily absorbed water to form $[\mathrm{Cu}(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2\mathrm{H_2O}]$.

$\mathrm{Cu}(\mathit{sucim})_2(\mathrm{OH_2})_2$ was obtained as a sky-blue powder by a procedure similar to that used for $\mathrm{Cu}(\mathit{sucim})_2(\mathit{py})(\mathrm{OH_2})$, using 10 g. (0.1 mol.) of succinimide, 3 g. (0.05 g. atom) of copper powder and 11 g. (0.1 mol.) of 2,6-lutidine.

Found: C, 33.1; H, 4.19; N, 9.73. Calcd. for $\mathrm{C_8H_{12}N_2O_6Cu}$: C, 32.5; H, 4.09; N, 9.47%.

All the compounds prepared in the present work, with the exception of $\mathrm{Cu}(\mathit{sucim})_2(\mathrm{OH_2})_2$, were soluble in chloroform, methylene dichloride, ethanol, methanol and pyridine, forming a greenish-blue or a dark-blue solution.

Pyridine, α-picoline and 2,6-lutidine, used as solvents for spectral measurements, were purified by distillation after having been dried over potassium hydroxide for several weeks.[3] The chloroform, which was purchased from Wako Co., was of extra-pure reagent grade, containing less than 0.05% water.

Measurements.—Quantitative dichroism measurements of the crystals were carried out at room temperature by Tsuchida and Kobayashi's microscopic method,[4] using polarized light in the visible and ultraviolet regions. The symbol α represents the absorption coefficient per mm. of a crystal. No correction was made for reflection on the surface of the crystal.

The absorption spectra of the compounds in organic solvents were determined at room temperature with a Beckman DU spectrophotometer.

Reflection spectra were determined with a Hitachi EPU 2A spectrophotometer. The symbols in the text are those conventionally used.

Results and Discussion

The Configuration of Bis(saccinimidato)copper(II) Complexes with Pyridine.—As has been discussed in a previous paper,[1] a succinimidate ion is combined with a copper(II)-ion through its nitrogen atom when this behaves as a unidentate (Fig. 1).

The electronic absorption spectra of bis(succinimidato)copper(II) complexes with pyridine are shown in Fig. 2. The absorption bands between 50 and $70\times10^{13}\,\mathrm{sec}^{-1}$ observed with $[\mathrm{Cu}(\mathit{sucim})_2(\mathit{py})_2]$ in the crystalline state are regarded as "ligand field bands" which are due to the *d-d* transitions.[1] The main band maximum (about $62\times10^{13}\,\mathrm{sec}^{-1}$) lies in a frequency region much higher than that of the cupric complexes of an ordinary kind. In the same way as in the previous paper,[1] the high frequency of the ligand field band maximum shows that $[\mathrm{Cu}(\mathit{sncim})_2(\mathit{py})_2]$ has a square-planar configuration of the $[\mathrm{Cu(N)_4}]$-type, with the fifth and the sixth co-ordination sites left vacant.

The crystal structure analysis of the complex

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[3] D. J. Royer, *J. Inorg. Nucl. Chem.*, **11**, 151 (1959).

[4] R. Tsuchida and M. Kobayashi, "The Colour and the Structure of Metallic Compounds" (Kinzokukagōbutsu no Iro to Kōzō), Zōshindo, Osaka (1944), p. 180.

TABLE I. ABSORPTION MAXIMA OF BIS(SUCCINIMIDATO)COPPER(II) COMPLEXES WITH PYRIDINE, PICOLINES AND LUTIDINES IN SOLID STATE

Complex	ν_{max} (half width)		Type
$Cu(\mathit{sucim})_2(\mathit{py})_2$	62*	52*	I $Cu(N)_4$ Red
$Cu(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})_2$	63.6 (15.1)	50.4 (11)	
$Cu(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2$	unstable		
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2$	unstable		
$Cu(\mathit{sucim})_2(2,4\text{-}\mathit{lut})_2\cdot 0.5H_2O$	61.8 (14.8)	50.0 (11)	
$Cu(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2$	unstable		
$Cu(\mathit{sucim})_2(\mathit{py})(OH_2)$	58.2*	53*	II $Cu(N)_3O$ Violet
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(OH_2)$	55.2 (14.4)	47 (sh)	
$Cu(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})(OH_2)\cdot CH_3OH$	unstable		IV $Cu(N)_3O_n$ Deep-blue
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(OH_2)_2\cdot CH_3OH$	unstable		
$Cu(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2\cdot 2H_2O$	50.8 (12.4)	44 (sh)	III $Cu(N)_4O_n$ Deep-blue
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2\cdot H_2O$	52.0 (14.5)	44 (sh)	
$Cu(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2\cdot H_2O$	51.2 (14.1)	44 (sh)	
$Cu(\mathit{sucim})_2(OH_2)_2$	45.0 (13.8)		Sky-blue

ν and half width: $10^{13}\,sec^{-1}$, *: in crystalline state, sh: shoulder

TABLE II. ABSORPTION MAXIMA OF BIS(SUCCINIMIDATO)COPPER(II) COMPLEXES WITH PYRIDINE, PICOLINES AND LUTIDINES IN CHLOROFORM SOLUTION

Complex	ν_{max}	$\log\varepsilon$	h. w.	Type
$Cu(\mathit{sucim})_2(\mathit{py})_2$	44	1.63	16.8	I
$Cu(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})_2$	44	1.61	18.5	
$Cu(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2$		unstable		
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2$	44	1.57	16.7	
$Cu(\mathit{sucim})_2(2,4\text{-}\mathit{lut})_2\cdot 0.5H_2O$	44	1.64	17.1	
$Cu(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2$		unstable		
$Cu(\mathit{sucim})_2(\mathit{py})(OH_2)$	44	1.63	17.6	II
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(OH_2)$	45	1.60	17.1	
$Cu(\mathit{sucim})_2(\alpha\text{-}\mathit{pic})(OH_2)\cdot CH_3OH$	45	1.63	21.0	IV
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})(OH_2)_2\cdot CH_3OH$		unstable		
$Cu(\mathit{sucim})_2(\beta\text{-}\mathit{pic})_2\cdot 2H_2O$	44	1.60	17.2	III
$Cu(\mathit{sucim})_2(\gamma\text{-}\mathit{pic})_2\cdot H_2O$	45	1.64	16.4	
$Cu(\mathit{sucim})_2(3,5\text{-}\mathit{lut})_2\cdot H_2O$	44	1.62	17.0	
$Cu(\mathit{sucim})_2(OH_2)_2$*	45	1.68	17.4	

* Alcohol solution, ν: $10^{13}\,sec^{-1}$, h. w.: half width in $10^{13}\,sec^{-1}$

is not yet available, and usually the planes of the complexes in the crystal are not exactly parallel to each other. However, it may readily be found that the A- and B-absorption in Fig. 2 represent the main features of the xy- and the z-absorption respectively of the square-planar complex, since previous studies have shown that, for ligand field absorption band, the xy-absorption has a larger oscillator strength than the z-absorption.[5]

The violet complex, $[Cu(\mathit{sucim})_2(\mathit{py})(OH_2)]$, in the crystalline state shows a peak at about $58.2\times10^{13}\,sec^{-1}$ which is remarkably dichroic and which is regarded as a ligand field band due to the cupric ion. The frequency at the band maximum is regarded as quite high for a cupric complex of the $[Cu(N)_3O]$-type. Thus, $[Cu(NH_3)_4]^{2+}$ and $[Cu\,\mathit{en}_2]^{2+}$ in water show absorption maxima at 49.2 and $54.6\times10^{13}\,sec^{-1}$ respectively. It is concluded that $[Cu(\mathit{sucim})_2(\mathit{py})(OH_2)]$ has a square-planar configuration of the $[Cu(N)_3O]$-type, with the fifth and the sixth sites left vacant.

The Configuration of Bis(succinimidato)copper(II) Complexes with Picolines and Lutidines.—The electronic absorption spectra of bis(succinimidato)copper(II) complexes with picolines and lutidines in the solid state were determined. An inspection of the data given in Table I indicates that there are three main types of succinimidato-copper(II) complexes with the amines, which are red, violet and deep-blue respectively. The difference in color between these types is so apparent that

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[5] S. Yamada and R. Tsuchida, *Ann. Reports Faculty of Sci., Osaka Univ.*, **4**, 79 (1956); This Bulletin, **29**, 289, 694 (1957).

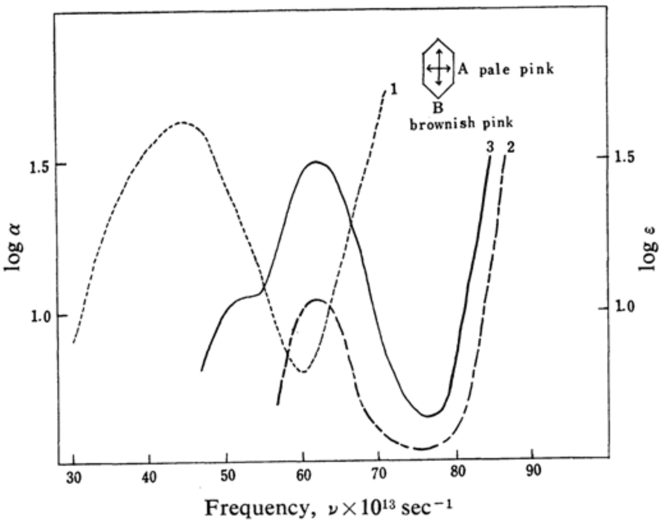

Fig. 2. Electronic absorption spectra of Cu$(sucim)_2(py)_2$ in the crystalline state and in chloroform.

1, soln.; 2, A-absorption in crystalline state; 3, B-absorption

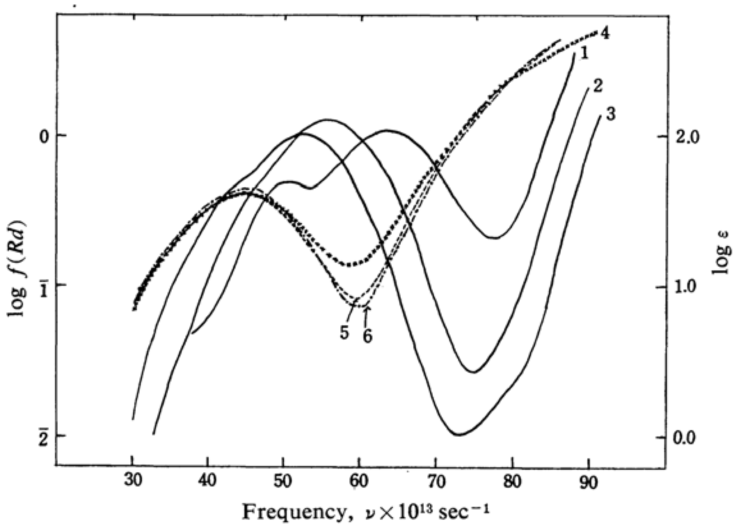

Fig. 3. Electronic absorption spectra of bis(succinimidato)copper(II) complexes in the solid state and in chloroform.

Cu$(sucim)_2(\alpha\text{-}pic)_2$ (1, solid; 4, soln.), Cu$(sucim)_2(\gamma\text{-}pic)(OH_2)$ (2, solid; 5, soln.) and Cu$(sucim)_2(\gamma\text{-}pic)_2\cdot H_2O$ (3, solid; 6, soln.). The solid spectra were determined by the reflection method.

in most cases it is possible to assign a compound to one of these types with little ambiguity (Table I). Besides these, there is a green type for α-picoline.

A typical spectrum of the red crystals is shown in Fig. 3. From the data in Table I, it is found that the red crystals show the main peak of the ligand field band at about $61.5\times 10^{13}\ \text{sec}^{-1}$ or at higher frequencies. The red crystals, which are denoted as type I, consist of square-planar complexes of the [Cu$(sucim)_2$(amine)$_2$]-type, since the frequency of the main peak of the ligand field band is exceedingly high.

The deep-blue or indigo crystals of type III show the peak of ligand field bands at about $50\times 10^{13}\ \text{sec}^{-1}$, a frequency which corresponds to a much lower frequency than the peak for the red, square-planar complexes of the [Cu$(N)_4$]-type. Thus, deep-blue crystals of [Cu$(sucim)_2(\beta\text{-}pic)_2\cdot 2H_2O$] and [Cu$(sucim)_2(\gamma\text{-}pic)_2\cdot H_2O$] show their ligand field bands at about 50.8 and $52.0\times10^{13}\,\mathrm{sec}^{-1}$, respectively (Table I). These frequencies are much lower than those of the square-planar complexes of the $[Cu(N)_4]$-type, and are very close to the values for the complexes, which have already been established to consist of a $[Cu(N)_4(O)_n]$-type, n being either one or two.1,6) It may be concluded that, in the crystals of $[Cu(sucim)_2(\beta\text{-}pic)_2\cdot 2H_2O]$ and $[Cu(sucim)_2(\gamma\text{-}pic)_2\cdot H_2O]$, one or two molecules of water occupy additional co-ordination sites above and below the $[Cu(N)_4]$-plane to form a quinque-co-ordinate, tetragonal-pyramidal or a sexa-co-ordinate, pseudo-octahedral complex of the $[Cu(N)_4(OH_2)_n]$-type.

The complexes classified as type IV may be interpreted in a similar way. It is most likely that in these complexes the methanol molecule is combined with the copper(II) ion, $[Cu(N)_3(O)_n]$ being thereby formed, where n is either two or three.

Of the compounds of type II, the pyridine compound, $[Cu(sucim)_2[(py)(OH_2)]$, has been discussed above. The violet compounds of type II reported in the present paper show the peak of the ligand field bands at about 55 to $59\times10^{13}\,\mathrm{sec}^{-1}$, a frequency which is slightly lower than the frequency for the red crystals but remarkably higher than the frequency for the complexes of the $[Cu(N)_4(OH_2)_n]$-type. It is, therefore, presumed that the violet crystals of type II consist of square-planar complexes of the $[Cu(sucim)_2(\text{amine})(OH_2)]$-type, in which the fifth and the sixth co-ordination sites around the copper(II) ion are left vacant.

In the case of α-picoline, a green type is also obtained when the red crystals of $[Cu(sucim)_2(\alpha\text{-}pic)_2]$ are left to stand in the atmosphere. The green type of the α-picoline complex shows a peak corresponding to the ligand field band at about $51.5\times10\,\mathrm{sec}^{-1}$; the band is, however, quite broad. It is most likely that the compound is polynuclear, with hydroxyl groups serving as bridges, judging from its properties. The detailed structure of the compound is not established in the present study. A similar procedure for the preparation of the red compound using 2,6-lutidine instead of the other lutidines or picolines gives none of the three types; instead, a pale-blue compound with an empirical formula of $Cu(sucim)_2(OH_2)_2$ was obtained. The pale-blue complex of $Cu(sucim)_2(OH_2)_2$ shows a ligand field band at about $45\times10^{13}\,\mathrm{sec}^{-1}$ which is comparatively symmetrical. Although the precise structure of the compound has not yet been completely clarified, the low frequency of the band maximum indicates that the compound consists of a sexa-co-ordinate complex of the $[Cu(N)_2(O)_4]$-type, with oxygen atoms of water molecules possibly serving as bridges.

It should be noted that the quadri-co-ordinate copper(II) complexes of type I show ligand field bands which are less symmetrical, with a shoulder on the lower frequency side of the main band. This fact may be understood mainly in terms of the symmetry of the complexes, since the tetragonal nature of the ligand field is regarded as more pronounced in the complexes of type I than in those of type II as well as of type III.

General Consideration.—It is to be noted that the red crystals of the $Cu(sucim)_2(pic)_2$ formula were isolated with all of the α-, β- and γ-picolines. The red crystals of all the compounds obtained are quite unstable, taking up molecules of water in the atmosphere to turn green in the case of the α-picoline and deep-blue in the case of the β- or γ-picoline complexes.

The red complexes of β- and γ-picoline readily take the fifth and the sixth ligands, while the corresponding complex of α-picoline does not. Moreover, the isolation of the blue crystals of the $[Cu(sucim)_2(\text{amine})_2(OH_2)_n]$-type is possible only with β- and γ-picolines, not with α-picoline. These facts may be understood mainly in terms of the steric factor.

The behavior of the lutidine-complexes of the $[Cu(sucim)_2(lut)_2]$-type may be interpreted in the same way as that of the corresponding complexes of picolines. Thus, the red 2,4-lutidine-complex in the atmosphere does not combine with a water molecule at the fifth or the sixth co-ordination sites; instead, the bond between the copper(II) ion and lutidine is readily broken, the original square-planar complex being changed into sky-blue $Cu(sucim)_2(OH_2)_2$. On the other hand, the red complex, $[Cu(sucim)_2(3{,}5\text{-}lut)_2]$, takes up one water molecule at the fifth site. The isolation of the blue crystals of the $[Cu(sucim)_2(lut)_2(OH_2)_n]$-type is found to be possible with those lutidines with no substituent on the α-carbon atom. This behavior is quite similar to that of the corresponding picoline-complexes of copper(II).

It should also be noted that the red pyridine-complex, $[Cu(sucim)_2(py)_2]$, has a much weaker tendency to combine additional ligands at the fifth and sixth co-ordination sites than do the complexes of the picolines and lutidines. Moreover, the square-planar, violet complex of $[Cu(sucim)_2(py)(OH_2)]$ is formed when the red $[Cu(sucim)_2(py)_2]$ is left in the air, but the corresponding violet complex is not formed with the picoline- or lutidine-complexes under the same conditions. Instead, the deep-blue complex of $[Cu(sucim)_2(pic)_2(OH_2)_n]$ or $[Cu(sucim)_2(lut)_2(OH_2)_n]$ is formed when the red

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6) S. Miki and S. Yamada, to be submitted shortly.

complex of the [Cu(*sucim*)$_2$L$_2$]-type is left in the atmosphere. The corresponding deep-blue complex was not isolated with pyridine. It seems certain that bis(succinimidato)copper(II) complexes of pyridine have a stronger tendency to keep the fifth and sixth co-ordination sites vacant. This difference between the pyridine complexes and the complexes of picolines may be ascribed to the nature of the copper(II)-ligand bond, since the steric factor alone can not explain these differences. A definite explanation of this is not given in the present paper, but it may be ascribed to the difference in the π-bonding contribution, if it is assumed, on the basis of the concepts presented previously, that the π-bonding is important in stabilizing the square-planar configuration with the fifth and the sixth sites left vacant.[1)]

The Configuration of Bis(succinimidato)copper(II) Complexes in Non-donor Solvents.—The electronic absorption spectra of red diaminebis(succinimidato)copper(II) complexes were examined in chloroform (Table II and Fig. 3). An enormous bathochromic shift of the ligand field band (about 18×10^{13} sec^{-1}) is observed on going from the solid to the solution. It is considered that the molecular configuration in the solid state is not present in the solution. Since Beer's law is obeyed, and since the solution is unchanged in several days, there is a very slight possibility of the decomposition of the complex. Moreover, the shift is much larger than that which would be expected if the solvent molecules were co-ordinated to the copper(II) ion, since the bonding of the solvent molecule with the copper(II) ion would be very weak. In the same way as has been discussed previously,[1)] it is considered that the molecule of [Cu(*sucim*$_2$)(amine)$_2$] in the solution is distorted from the square-planar configuration.

The violet and deep-blue complexes of types II and III also show ligand field bands at about 44 and 45×10^{13} sec^{-1}. The observed bathochromic shift on going from the solid to the solution is quite remarkable for the shift expected if the co-odination of chloroform molecules to the cupric ion takes place. It is considered that the field produced by ligands surrounding the copper(II) ion is distorted from the tetragonal symmetry to a considerable extent.

The bathochromic shift on going from the solid to the solution in the case of type III is considerably smaller than that in the case of types I and II, although the shift in the former case is still so great that some configurational change is to be assumed. A detailed discussion of them will be deferred until more materials become available.

The absorption spectra of these complexes in methylene dichloride are quite similar to those in chloroform. The molecular configuration of these complexes, therefore, is considered to be similar in all these solvents.

The absorption spectra of the compounds of type I in ethanol are similar to the spectra of the compounds in chloroform. Therefore, the same conclusion as that above is obtained. On the contrary, the absorption spectra of the complexes of types II and III in ethanol are more complicated, and the discussion of them will be deferred until more materials become available.

The Configuration of Bis(succinimidato)copper(II) Complexes in Pyridine, Picolines and Lutidines.—In donor solvents such as pyridine, the situation may be different from that in non-donor solvents. The red bis(pyridine)bis(succinimidato)copper(II) in pyridine shows a ligand field band at about $47\sim48\times10^{13}$ sec^{-1}, a frequency which is much higher than that (about 44×10^{13} sec^{-1}) of the same compound in non-donor solvents. It may thus be inferred that the pyridine molecules are probably bound with the copper(II) ion to complete its sexa-co-ordination, the tetragonal symmetry of the ligand field being kept.

On the contrary, the red complexes of type I in 2,6-lutidine show a ligand field band at about 58×10^{13} sec^{-1}, a frequency which is much higher than those of the same compounds in pyridine as well as in other non-donor solvents (Fig. 4). It is most certain, from the steric ground, that the molecules of 2,6-lutidine are not bound with the copper(II) ion in the same sense as the molecules of pyridine are bound. The high frequency of the band maximum of the complex in 2,6-lutidine (Fig. 4) is taken as indication that the symmetry of the ligand field around the copper(II) ion is tetragonal,

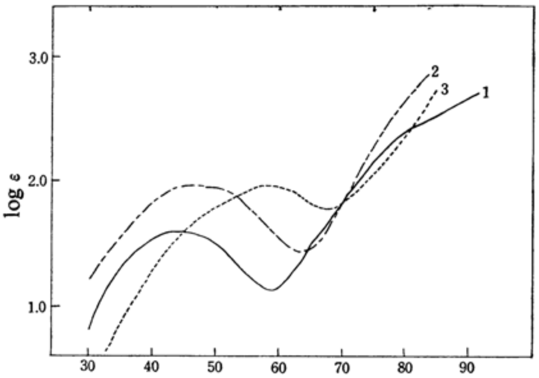

Fig. 4. UV-spectra of Cu(*sucim*)$_2$(α-*pic*)$_2$ in organic solvents.

1, Chloroform; 2, Pyridine; 3, 2,6-Lutidine and that the slight bathochromic shift of the band maximum relative to the band maximum of the crystal may be due to a feeble effect of the 2, 6-lutidine molecules on the copper(II) ion. It is likely that the 2, 6-lutidine molecules point toward the copper(II) ion at a farther distance in such a way that the ligand field around the copper(II) ion keeps the tetragonal symmetry.

Summary

Bis(succinimidato)copper(II) complexes with pyridine and its derivatives have been prepared, the derivatives involving α-, β- and γ-picoline, 2, 4-lutidine and 3, 5-lutidine. Depending upon the reaction conditions the following types of complexes have been obtained: (1) red complexes of $[\mathrm{Cu}(sucim)_2(\mathrm{amine})_2]$, (2) violet complexes of $[\mathrm{Cu}(sucim)_2(\mathrm{amine})(\mathrm{OH}_2)]$, and (3) indigo or dark-blue complexes of $[\mathrm{Cu}(sucim)_2(\mathrm{amine})_2(\mathrm{OH}_2)_n]$. When 2, 6-lutidine is employed, however, none of the three types is obtained; rather, a blue compound with the formula of $\mathrm{Cu}(sucim)_2(\mathrm{OH}_2)_2$ is isolated.

The configuration of the three types of complexes has been examined, mainly on the basis of the electronic absorption spectra. The complexes of types 1 and 2 consist of quadri-coordinate complexes with a square-planar configuration. The compounds of type 3 consist of quinque- or sexa-co-ordinate complexes.

The configuration of these complexes of the three types in non-donor solvents has also been discussed.

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